



# Atomically isolated copper on titanium dioxide for ammonia photosynthesis via nitrate reduction with unprecedentedly high apparent quantum yield

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## ARTICLE INFO

### Keywords:

Solar fuel production  
Single-atom catalyst  
2D nanosheet structure  
Hydrogen carrier  
Photocatalysis

## ABSTRACT

Photocatalytic nitrate ( $\text{NO}_3^-$ ) reduction to  $\text{NH}_3$  (PcNRA) is a sustainable alternative that is considered advantageous over  $\text{N}_2$  fixation, which suffers from the high dissociation energy and sluggish activation of inactive  $\text{N}_2$ . Although PcNRA has recently been shown to achieve excellent selectivity, its sluggish kinetics restrict the  $\text{NH}_3$  production efficiency. Herein, we present a single-atom Cu-incorporated  $\text{TiO}_2$  nanosheet (Cu-TNS) photocatalyst for efficient and selective PcNRA. Single Cu atoms displacing Ti sites accumulate photogenerated electrons, ensuring efficient charge separation and surface  $\text{NO}_3^-$  reduction. Moreover, introducing Cu atoms into the  $\text{TiO}_2$  matrix induces spontaneous defect formation, resulting in oxygen vacancies and lattice strain that promote  $\text{NO}_3^-$  adsorption and activation. The simultaneous presence of single Cu atoms and structural defects in Cu-TNS synergistically stimulates PcNRA, leading to a 62-fold enhancement over pristine  $\text{TiO}_2$  in  $\text{NH}_3$  production with 97.6% selectivity and an unprecedentedly high apparent quantum yield of 11.7% at 330 nm under optimized conditions.

## 1. Introduction

Ammonia ( $\text{NH}_3$  or  $\text{NH}_4^+$ ), one of the most produced and utilized chemicals, is an indispensable feedstock for nitrogen-based fertilizers and is recently considered an ideal carbon-neutral fuel or hydrogen carrier with an intensely high hydrogen density [1–3]. Unfortunately, current  $\text{NH}_3$  manufacturing primarily relies on the energy-consuming (1.0–2.0% of the world's energy output) and waste-intensive (1.5% of the world's carbon emission) Haber-Bosch process [4,5]. Among the environmentally-friendly and thus sustainable alternatives,

photocatalytic nitrate ( $\text{NO}_3^-$ ) reduction to ammonia (PcNRA) is a favorable opportunity for green  $\text{NH}_3$  production. The relatively low dissociation energy of the  $\text{N}=\text{O}$  bond ( $204 \text{ kJ mol}^{-1}$ ) and the high aqueous solubility of  $\text{NO}_3^-$  could readily exempt the fatal bottleneck of  $\text{N}_2$  fixation [6–8] and sufficient  $\text{NH}_3$  yields eliminate the possibility of false positives [9,10]. As another virtue,  $\text{NO}_3^-$  as well as general organic matters acting as hole scavengers are abundantly prevalent as major pollutants in wastewater [11,12]. Therefore, PcNRA, which degrades contaminants via sunlight to produce value-added chemicals and accelerates reaction kinetics, offers a promising avenue to simultaneously

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<https://doi.org/10.1016/j.apcatb.2023.123185>

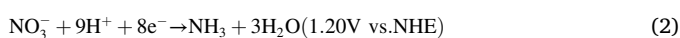
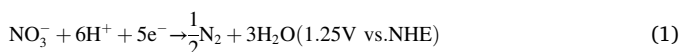
Received 5 July 2023; Received in revised form 15 August 2023; Accepted 16 August 2023

Available online 18 August 2023

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address energy and environmental concerns [13].

PcNRA has two possible pathways:  $\text{N}_2$  formation via  $5\text{e}^-$  reduction (Eq. (1)) and  $\text{NH}_3$  formation via  $8\text{e}^-$  reduction (Eq. (2)) [14]. The hydrogen evolution reaction (Eq. (3)), a fierce side-reaction that consumes photoexcited electrons, is another consideration [15,16]. Accordingly, PcNRA is thermodynamically and kinetically unfavorable, and thus the majority of previous  $\text{NO}_3^-$  reduction studies have been focused on  $\text{N}_2$  formation as a water treatment [17–19]. To the best of our knowledge, only a few photocatalysts for selective PcNRA, such as titanium dioxide ( $\text{TiO}_2$ ) with surface oxygen vacancies (OVs) [14] or decorated with metallic [20], bimetallic [21] or metal oxide [22,23] clusters, have been reported. Although 96–98% selectivity toward  $\text{NH}_3$  synthesis has been reported, the actual catalytic activities have still been far below the practical standard due to the sluggish reaction kinetics (the highest apparent quantum yield (AQY) of 3.5% (at  $\lambda = 525 \text{ nm}$ )) [22]. Therefore, the design of an efficient photocatalyst for selective  $\text{NH}_3$  production is highly desirable.



Recently, single-atom catalysts (SACs) have been intensely investigated as a breakthrough in the inefficiency of photocatalysis because the isolated metal atoms provide more active sites and reactant-molecule adsorption [24,25]. So far, although SACs have been studied for various photocatalysis such as  $\text{H}_2$  evolution [26–28],  $\text{CO}_2$  conversion [29] and organic pollutant degradation [30,31], the impact of SACs on PcNRA has not yet been fully exploited. Among the SAC candidates, Cu, one of the earth-abundant transition metals, has shown impressive selectivity and activity for photo-/electrochemical  $\text{NH}_3$  synthesis due to its unique properties [20,21,32,33]. Its volatile valence state ensures efficient charge separation, leading to higher catalytic activity compared to even noble metal-loaded photocatalysts [34]. Therefore, incorporating Cu atoms into a light-responsive metal oxide lattice could be a guaranteed strategy to maximize the catalytic activity and selectivity of SACs for PcNRA. Moreover, this strategy may induce the formation of OVs and lattice strain due to the different valence states of the metal and support, which further stimulates adsorption and activation of the reactant-molecules [35,36].

Following the above hypothesis, we designed and synthesized single-atom Cu-introduced  $\text{TiO}_2$  nanosheets (Cu-TNS) for efficient and selective PcNRA under ambient conditions. Through a bottom-up approach, single Cu atoms were uniformly distributed in the  $\text{TiO}_2$  matrix by displacing Ti sites. The site-specific-incorporated single Cu atoms exhibited a high oxidation state resulting from a high unoccupied state level, which induced the localization of photogenerated electrons at the single Cu sites, effectively boosting charge separation. In particular, structural defects such as OV and lattice strain spontaneously occurred in the vicinity of stabilized Cu atoms, which delivered favorable  $\text{NO}_3^-$  adsorption sites and thereby eliminated the activation barrier. Thanks to the concurrent existence of single Cu atoms and defects in the  $\text{TiO}_2$  matrix, Cu-TNS exhibited a 62-fold enhanced  $\text{NH}_4^+$  production rate with 97.6% selectivity compared to pristine  $\text{TiO}_2$  nanosheets (TNS). Moreover, Cu-TNS exhibited an AQY of 11.7% at 330 nm under optimized reaction conditions, far surpassing that of the current state-of-the-art photocatalyst for PcNRA [22].

## 2. Experimental section

### 2.1. Materials

Tetrabutyl titanate (TBOT,  $\geq 99.0\%$ ), copper nitrate trihydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , 99.9%), hydrofluoric acid (HF, 37 wt%), iodine ( $\text{I}_2$ ,

99.5%), acetone ( $\text{CH}_3\text{COCH}_3$ , 96%), methanol ( $\text{CH}_3\text{OH}$ ,  $\geq 99.0\%$ ), ethylene glycol (anhydrous, 99.8%) formic acid ( $\text{HCOOH}$ ,  $\geq 95.0\%$ ), potassium nitrate ( $\text{KNO}_3$ ,  $\geq 99.0\%$ ), potassium nitrate- $^{15}\text{N}$  ( $\text{K}^{15}\text{NO}_3$ , 98 atom%), potassium sulfate ( $\text{K}_2\text{SO}_4$ ,  $\geq 99.0\%$ ), maleic acid ( $\text{C}_4\text{H}_4\text{O}_4$ ,  $\geq 99.0\%$ ), ammonium chloride ( $\text{NH}_4\text{Cl}$ ,  $\geq 99.5\%$ ), and ammonium- $^{15}\text{N}$  chloride ( $^{15}\text{NH}_4\text{Cl}$ ,  $\geq 98$  atom%) were purchased from Sigma Aldrich. Absolute ethanol was purchased from Fisher Scientific Korea Ltd. (Seoul, Korea). All chemicals were obtained from commercial suppliers and used without further purification.

### 2.2. Photocatalysts synthesis

The Cu-TNS, oxygen-deficient  $\text{TiO}_2$  nanosheets (OV-TNS), and pristine  $\text{TiO}_2$  nanosheets (TNS) photocatalysts were synthesized by using the solvothermal method [37] with modifications. In a typical synthetic process, 5 mL of TBOT were mixed with 0.6 mL of HF, 20 mL of absolute ethanol, and a calculated amount of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (a specific at% of Cu relative to Ti), followed by stirring for 30 min. The solution was then transferred into a Teflon-lined stainless steel autoclave and heated in an oven at  $180^\circ\text{C}$  for 4 h. The final product was centrifuged, washed repeatedly with DI water, and dried at  $60^\circ\text{C}$  overnight. OV-TNS was synthesized following the above procedure without  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , where oxygen vacancies are present due to the nature of the 2D nanosheet structure [35]. TNS was synthesized by calcination of OV-TNS at  $300^\circ\text{C}$  for 2 h to remove oxygen vacancies and obtain higher crystallinity. A CuNP/TNS photocatalyst was prepared via photo-reduction method. 50 mg of TNS was dispersed in 25 mL of 20 vol% aqueous methanol solution, containing 4.7 mg (3 at%) of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ . The mixture was stirred for 1 h under dark condition to achieve adsorption/desorption equilibrium. The suspension was then irradiated with 300-W Xe lamp (Newport) for 6 h under vigorous stirring. The final product was centrifuged, washed with DI water and finally dried at  $60^\circ\text{C}$  overnight.

### 2.3. Characterization, calculation, and photocatalytic reaction

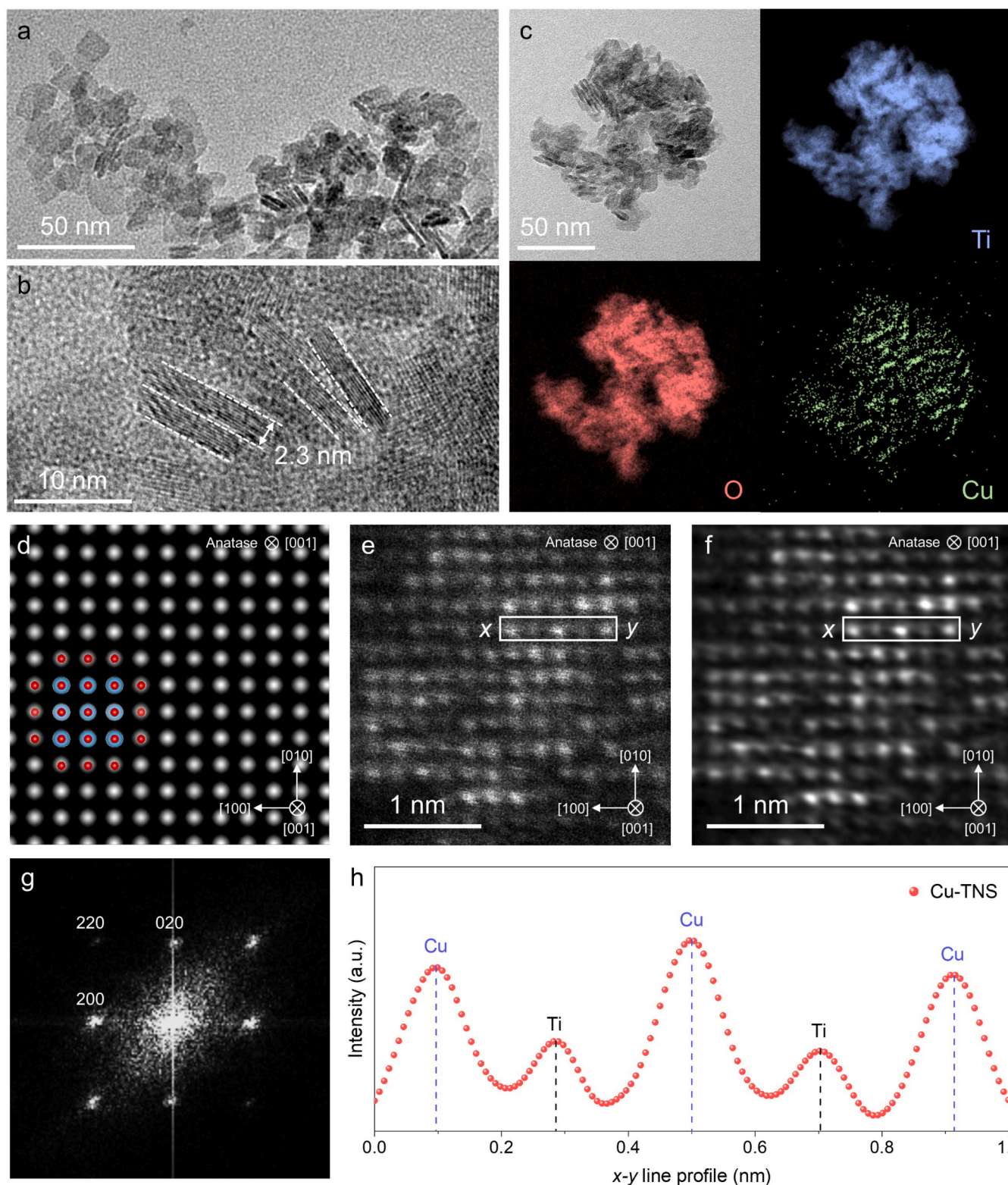
The characterization, calculation, and photocatalytic reaction details for the prepared catalysts are described in the [Supporting Information](#).

## 3. Results and discussion

### 3.1. Characterization of Cu-TNS

Cu-TNS and counterpart photocatalysts, pristine TNS and OV-TNS, were prepared using a facile solvothermal method to substantiate the contributions of each feature. The morphology of Cu-TNS was investigated via transmission electron microscopy (TEM) and scanning electron microscopy, revealing ultra-thin nanosheet structures with a lateral length of  $\sim 10 \text{ nm}$  and a thickness of  $\sim 2.3 \text{ nm}$  (Fig. 1a, b and Fig. S1). Lattice spacing measurements in the high-resolution (HR)TEM images reveal that the top and bottom facets are the (001) planes and the side facets are the (200) and (020) planes of anatase  $\text{TiO}_2$ , indicating that reactive (001) facets [37] are predominantly exposed in Cu-TNS (Fig. S2). Electron energy loss spectroscopy and scanning TEM energy dispersive X-ray spectroscopy (STEM-EDS) analyses show an even distribution of Cu species on the TNS without aggregation (Fig. 1c and Fig. S3). TNS and OV-TNS without Cu species have similar nanosheet structures, of which TNS is slightly larger with distinct grain contours due to high crystallinity without defects (Figs. S4–6), which is consistently evidenced by the slightly reduced surface area of TNS (Fig. S7).

High-angle annular dark-field (HAADF)-STEM analysis was performed to gain in-depth insight into the localized atomic structure of Cu-TNS. The bright contrast spots evident at the Ti atomic sites imply that the Cu atoms in the Ti vacancies are particularly stable and other configurations such as clusters or new phases did not occur (Fig. 1d–g). The corresponding line scan profile of the marked area further affirms

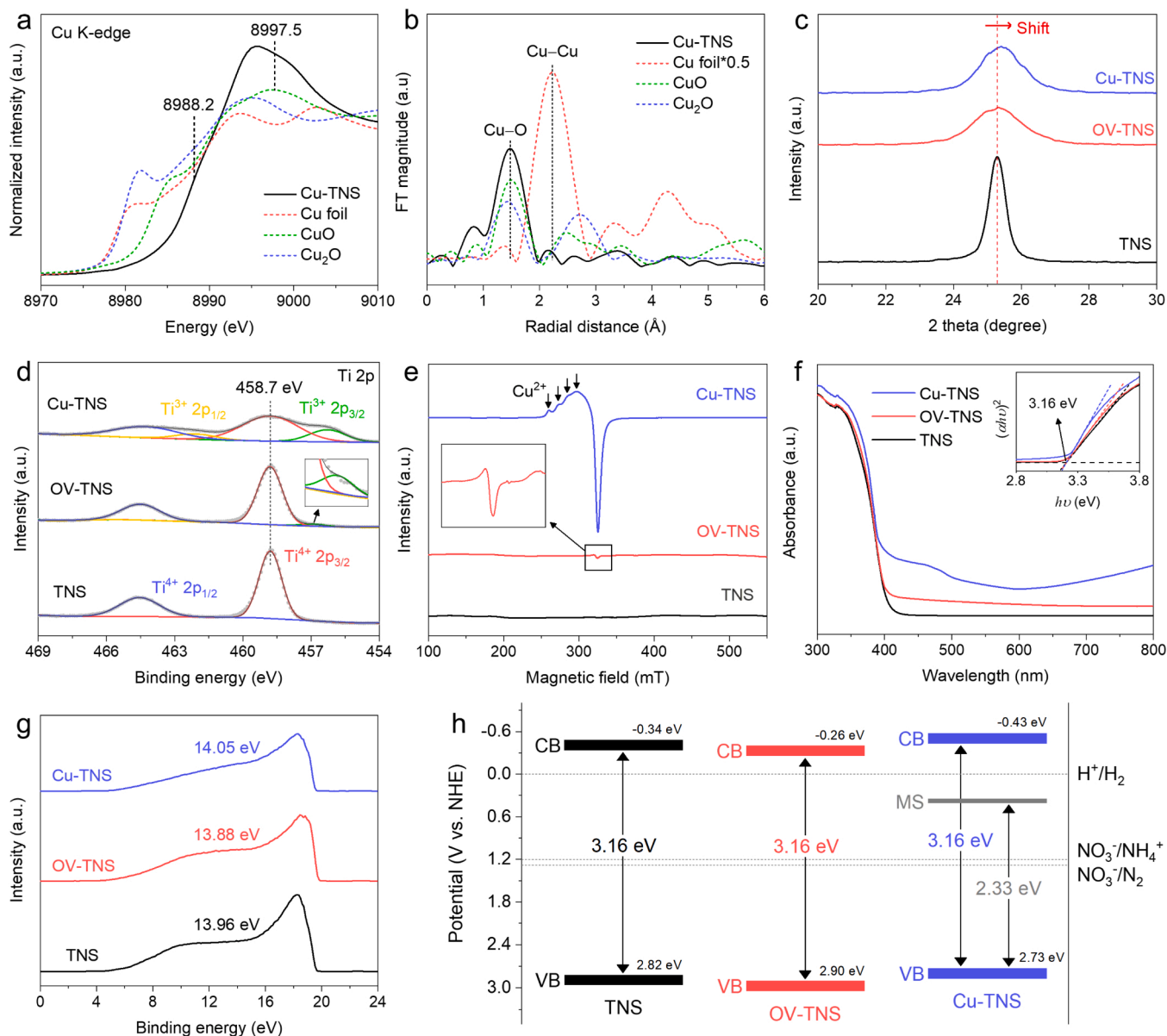


**Fig. 1.** Representative (a), (b) TEM images and (c) an EELS elemental mapping (Ti, O and Cu) image of Cu-TNS. HAADF-STEM images of Cu-TNS in the [001] direction: (d) a simulated image of anatase  $\text{TiO}_2$  showing the corresponding anatase  $\text{TiO}_2$  unit cell structure in which the blue and red spheres represent Ti and O, respectively; (e) a Cs-corrected raw image; (f) a filtered image and (g) the corresponding fast Fourier transform pattern. (h) The x–y line scan profile of the marked areas in (e) and (f).

distinct intensity differences that suggest stabilization of the Cu atoms in the  $\text{TiO}_2$  matrix by forming Cu—O—Ti bonds (Fig. 1h). Subsequently, X-ray absorption spectroscopy (XAS) was performed to statistically analyze the comprehensive atomic structure of Cu-TNS. The Cu K-edge

X-ray absorption near-edge structure (XANES) spectrum in Fig. 2a exhibits the typical characteristic absorption edges of the  $\text{Cu}^{2+}$  valence state [26] at 8988.2 and 8997.5 eV. Moreover, the  $\text{Cu}^0$  and  $\text{Cu}^{1+}$  valence states in Cu-TNS were not present, unlike in the reference XANES spectra





**Fig. 2.** (a) Cu K-edge XANES spectra and (b) Fourier-transformed *R*-space EXAFS of Cu-TNS with the references (Cu foil, CuO and Cu<sub>2</sub>O). (c) Magnified XRD patterns, (d) Ti 2p XPS spectra (inset: enlarged Ti<sup>3+</sup> 2p<sub>3/2</sub> peak of OV-TNS), (e) EPR spectra (inset: enlarged EPR spectrum of OV-TNS) and (f) UV-visible DRS spectra (inset: the corresponding Tauc plots using  $(\alpha h\nu)^2$  as a function vs. the photon energy, where  $\alpha$  is the absorption coefficient,  $h$  is the Planck's constant,  $\nu$  is the light frequency) of TNS, OV-TNS and Cu-TNS. (g) UPS spectra with corresponding peak widths and (h) the band structure alignments in TNS, OV-TNS and Cu-TNS. The bandgap energy ( $E_g$ ) of Cu-TNS from the Tauc plot is 3.16 eV. The valence band energy values were calculated using He I excitation energy (21.22 eV) and the UPS width. The conduction band energy values were calculated using the obtained bandgap and valence band energies. All energy vs. vacuum values were converted to vs. NHE using the following relationship:  $E_{\text{vacuum}} = -E_{\text{NHE}} - 4.44$  eV.

of Cu foil and Cu<sub>2</sub>O. It is noteworthy that the single Cu atoms exhibited a high oxidation state originating from a high unoccupied state level, thereby implying its high electron-accepting capacity. Fourier transformation of the extended X-ray absorption fine structure (EXAFS) of Cu-TNS shows only one characteristic peak at  $\sim 1.5$  Å corresponding to the Cu—O scattering path, indicating that the Cu atoms in the 2+ oxidation state had been stabilized at the Ti sites and were coordinated with the oxygen atoms in the lattice (Fig. 2b). The absence of the Cu—Cu scattering path at  $\sim 2.2$  Å verifies that Cu-TNS was substantially free from Cu clustering.

After acquiring proof of single Cu atoms occupying the Ti sites, the spontaneous formation of OV and lattice distortion was investigated. The Ti K-edge XANES spectra of TNS, OV-TNS, and Cu-TNS in Fig. S8a and S8b are analogous with three pre-edge peaks associated with

anatase TiO<sub>2</sub> (labeled P1, P2, and P3), corresponding to the enabling of quadruple 1s→3d transitions [35]. The intensity escalation in P2 for OV-TNS and Cu-TNS implies Ti site distortion due to the introduction of Cu atoms and/or OV into the lattice. By comparing reference Ti configurations with different valence states, the OV concentrations in OV-TNS and Cu-TNS were calculated as 2.21% and 9.89%, respectively (Fig. S9 and Table S1). The abundant OV concentration in Cu-TNS indicates that incorporation of Cu atoms into Ti atomic sites induces spontaneous OV formation due to the different valence states of Ti and Cu. Fourier transformation of the EXAFS spectrum of the *R*-space reveals that the Ti—O scattering path for OV-TNS and Cu-TNS decreased in intensity and shifted to shorter distances, suggesting abatement of the Ti—O coordination number owing to the formation of OV and Ti<sup>3+</sup> (Fig. S8c). Furthermore, the X-ray diffraction (XRD) patterns of the



prepared photocatalysts in Fig. S10 exhibit typical peaks attributed to anatase  $\text{TiO}_2$  (JCPDS-21-1272), with differences in intensity depending on the presence or absence of defects. Interestingly, the anatase (101) reflection plane of Cu-TNS shifted to a higher number of  $2\theta$  degrees, strongly implying that the lattice strain had become constricted (Fig. 2c) due to the presence of the interstitial  $\text{Cu}^{2+}$  sites inside the  $\text{TiO}_2$ . The lattice strain was calculated using the Voigt method as  $-0.705\%$  for Cu-TNS (Table S2), revealing that although the atomic radius of  $\text{Cu}^{2+}$  ( $0.73 \text{ \AA}$ ) is larger than that of  $\text{Ti}^{4+}$  ( $0.61 \text{ \AA}$ ), Cu atomic incorporation inside the  $\text{TiO}_2$  lattice constitutes a negative strain due to OV formation leading to Jahn-Teller compression [35]. Structural defects in the lattice were also evidenced via HAADF-STEM analysis (Figs. S11 and S12). The atomic structure of TNS is well-aligned whereas severe distortion was observed in Cu-TNS. Line scan profiles reveal that the length of the atomic array consisting of both Ti and Cu is shorter than that of the pristine Ti-only atomic array.

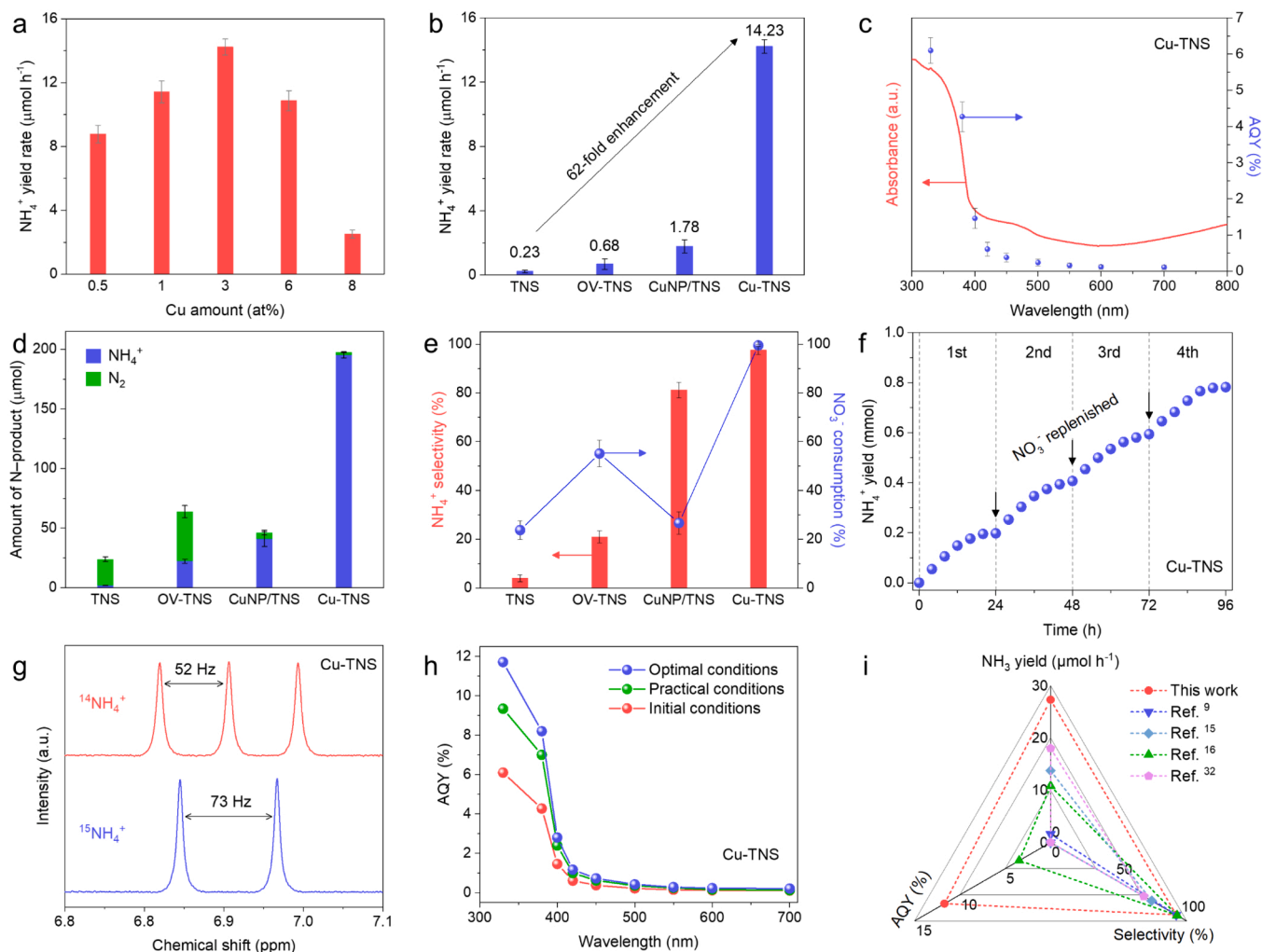
The defects in OV-TNS and Cu-TNS were further examined by using X-ray photoelectron spectroscopy (XPS) (Fig. 2d and Fig. S13) and electron paramagnetic resonance (EPR) (Fig. 2e and Fig. S14). The deconvoluted high-resolution Ti 2p XPS spectra of TNS and OV-TNS contain typical characteristic peaks for  $\text{Ti}^{4+}$ , with that of OV-TNS having a slight rise of additional  $\text{Ti}^{3+}$  characteristic peaks, which is the result of OV and  $\text{Ti}^{3+}$  presence. In the case of Cu-TNS, distinct  $\text{Ti}^{3+}$  peaks appeared, implying higher concentration of OVs and  $\text{Ti}^{3+}$  due to the incorporation of Cu atoms. The high-resolution O 1s XPS spectra of Cu-TNS are also distinct from OV-TNS and TNS in terms of the shift in lattice oxygen peak and the increased area of OV-associated peak due to the Cu atom incorporation and coordination with neighboring O atoms. The results from the EPR spectra are with those from the XPS analysis by revealing a faint signal for TNS with distinct signals at  $g = \sim 1.998$  (OV) and  $\sim 2.003$  ( $\text{Ti}^{3+}$ ) for Cu-TNS. Although the spectrum for OV-TNS likewise shows two signals representing OV and  $\text{Ti}^{3+}$ , their intensities are noticeably smaller than those in the spectrum for Cu-TNS, which indicates lower concentration of OVs and  $\text{Ti}^{3+}$  in the absence of Cu atoms. It is noteworthy that the spectrum for Cu-TNS exhibits an asymmetric resonance line arising from the anisotropic hyperfine structure of  $\text{Cu}^{2+}$  ions, and related EPR simulations further reveal that the asymmetric resonance line consists of two components: interstitial  $\text{Cu}^{2+}$  sites inside the  $\text{TiO}_2$  lattice and the  $\text{Cu}^{2+}$  species on the surface (Fig. S15). The XPS and EPR results are consistent with the aforementioned XAS, XRD, and HAADF-STEM results, confirming defect formation by the introduction of single Cu atoms.

The optical properties and band structures of the prepared photocatalysts (vital for analyzing their efficiencies) were determined by using UV-visible diffuse reflectance (DRS) and UV photoelectron spectroscopy (UPS). The UV-visible DRS spectra reveal that TNS exhibits a sharp edge at  $\sim 390 \text{ nm}$ , corresponding to the interband transition of anatase  $\text{TiO}_2$  (Fig. 2f). Meanwhile, those of OV-TNS and Cu-TNS exhibit enhanced absorption in the visible light region due to the presence of defects. That of Cu-TNS with isolated Cu atoms further exhibits step-like absorption at  $\sim 480 \text{ nm}$  and a broad band at  $\sim 700 \text{ nm}$ , reflecting the generation of the mid-gap state (MS) and  $d-d$  transition in Cu [26], respectively. Nevertheless, the estimated intrinsic bandgaps of TNS, OV-TNS, and Cu-TNS were still identical ( $3.16 \text{ eV}$ ), as determined from their converted UV-visible spectra (the inset of Fig. 2f). The additional bandgap corresponding to the electronic transition between the valence band (VB) and MS of Cu-TNS was identified as  $2.33 \text{ eV}$  (Fig. S16). The ionization potential or the VB energy was measured from the UPS spectra in Fig. 2g and Fig. S17 by subtracting the peak width from the He I excitation energy ( $21.22 \text{ eV}$ ). The band positions of TNS, OV-TNS, and Cu-TNS were identified by employing the obtained bandgap and VB energy values (vs. NHE), (Fig. 2h). In particular, the conduction band (CB) energy of Cu-TNS is more negative than its counterparts, signifying that PcNRA is more efficient with Cu-TNS from a thermodynamic perspective.

### 3.2. Photocatalytic $\text{NH}_4^+$ production

The PcNRA experiments were conducted in an aqueous  $\text{NO}_3^-$  solution under full-spectrum irradiation (see Supporting Information) and mainly quantified using ion chromatography (Figs. S18 and S19). Formic acid ( $\text{HCOOH}$ ) was selected as an electron donor or simulated organic matter due to its abundance in wastewater and its ability for  $\text{NH}_3$  synthesis via formation of carboxyl anion radicals with strong reducing capability [14,38]. For optimization of the Cu content, Cu-TNS with various at% of Cu to Ti were synthesized and the actual wt% of Cu was analyzed by inductively coupled plasma atomic emission spectroscopy (Table S3). All of the prepared Cu-TNS samples provided attractive  $\text{NH}_4^+$  yields regardless of the at% of Cu (Fig. 3a), as well as optical modulation which may be indicative of a reversible  $\text{Cu}^{2+}/\text{Cu}^{1+}$  reduction process ( $0.16 \text{ eV}$  vs. NHE) with lattice tuning by atomically localized photoelectrons at isolated Cu sites (Fig. S20) [26,27]. Among them, the 3 at% (1.95 wt%) Cu sample had the highest  $\text{NH}_4^+$  photosynthesis activity and was thus selected for further study. The basis of the relatively inferior activities of the 6 at% and 8 at% Cu samples was the formation of new configurations such as clusters or  $\text{CuO}$  phases, as unveiled via XAS and XRD analyses (Fig. S21). In addition, Cu metal nanoparticle-deposited TNS ( $\text{CuNP/TNS}$ ) was prepared via a photo-deposition method to explicitly examine the benefits of SAC over metal cluster catalysts for PcNRA. The outcomes of relevant analyses such as TEM, XAS, XRD, and XPS validated the successful synthesis of the  $\text{CuNP/TNS}$  catalyst (Figs. S22–S24). During the 2-h PcNRA experiment, the three modified TNS catalysts exhibited at least triple the activity of TNS for  $\text{NH}_4^+$  production, indicating that the presence of Cu and/or OVs improves the surface catalytic activity of  $\text{TiO}_2$  to facilitate  $\text{NH}_3$  photosynthesis (Fig. 3b). Notably, the  $\text{NH}_4^+$  yield rate of Cu-TNS was significantly increased by 62-fold compared to TNS, demonstrating the impressive effect of SAC on PcNRA. The wavelength-dependent AQY of Cu-TNS showed a trend consistent with the optical absorption spectrum and reached its highest value of 6.1% at  $330 \text{ nm}$  (Fig. 3c). This consistency secures the knowledge that the reaction is indeed the photo-driven  $\text{NO}_3^-$ -to- $\text{NH}_3$  conversion of the catalyst, which is further supported by negligible  $\text{NH}_4^+$  production in the control experiments (Fig. S25).

Subsequently, the PcNRA selectivity (another pivotal aspect of this study) was investigated (Fig. 3d and Fig. S26). After 24 h of PcNRA employing Cu-TNS,  $199.98 \text{ }\mu\text{mol}$  of the supplied  $\text{NO}_3^-$  in the reaction solution was reduced, leaving only  $1.15 \text{ }\mu\text{mol}$  from the initial amount ( $201.14 \text{ }\mu\text{mol}$ ). Meanwhile,  $195.06 \text{ }\mu\text{mol}$  of  $\text{NH}_4^+$  was produced from the  $\text{NO}_3^-$  reduction process, indicating that most of the N molecules had been selectively converted to  $\text{NH}_4^+$ . The  $\text{NH}_4^+$  yield rate remained linear for the first few hours but then gradually diminished over time due to the depletion of  $\text{NO}_3^-$ . The  $\text{NH}_4^+$  yield scarcely changed during the last 4 h of the reaction, suggesting that the produced  $\text{NH}_4^+$  was not oxidized back to  $\text{N}_2$  by the photoholes. Nitrite ions (one of the most common by-products of  $\text{NO}_3^-$  reduction) [14,22,33] were not detected throughout the reaction, and the total amount of N species remained nearly identical during the reaction, inferring that the only N-species products of photocatalytic  $\text{NO}_3^-$  reduction were  $\text{NH}_4^+$  and  $\text{N}_2$ . Compared with TNS, OV-TNS, and  $\text{CuNP/TNS}$  exhibit enhanced activity in terms of  $\text{NO}_3^-$  reduction and selective  $\text{NH}_4^+$  production, respectively, demonstrating that the OVs serve as a favorable  $\text{NO}_3^-$  adsorption site and the Cu species play a decisive role in selective  $\text{NH}_4^+$  production. Still,  $\text{CuNP/TNS}$  provided a considerable  $\text{N}_2$  yield compared to Cu-TNS, which can be postulated by the multiple adsorption sites for  $\text{NO}_3^-$  on the metal particles increasing the possibility of N–N bonding [39]. Cu-TNS exhibits significantly enhanced activity for both  $\text{NO}_3^-$  reduction and selective  $\text{NH}_4^+$  production compared to its counterparts thanks to the synergistic effect of Cu atom incorporation and spontaneous defect formation. Consequently, Cu-TNS achieved 97.6% for  $\text{NH}_4^+$  selectivity from an N-species conversion viewpoint (see Supporting Information) when  $> 99\%$  of  $\text{NO}_3^-$  was consumed (Fig. 3e and Table S4), confirming both selective and outstanding PcNRA performance.



**Fig. 3.** (a) The  $\text{NH}_4^+$  yield rate of Cu-TNS after the first two hours of PCNRA depending on the Cu amount. (b) The  $\text{NH}_4^+$  yield rate of TNS, OV-TNS, CuNP/TNS and Cu-TNS after the first two hours of PCNRA. (c) Wavelength-dependent AQY of Cu-TNS for PCNRA vs. light absorption. (d) The amounts of N-species products after 24 h of PCNRA. (e)  $\text{NH}_4^+$  selectivity in terms of N-species conversion and  $\text{NO}_3^-$  consumption after 24 h of PCNRA. (f) Long-term PCNRA stability testing of Cu-TNS. The  $\text{NH}_4^+$  yield rate gradually decreased over the 24-hour cycle due to the depletion of  $\text{NO}_3^-$ . At the end of each 24-h cycle,  $\text{NO}_3^-$  supplementation restored the yield rate of  $\text{NH}_4^+$  to its initial level. (g)  $^1\text{H}$  NMR spectra of the  $\text{NH}_4^+$  generated after 12 h of PCNRA using Cu-TNS with  $\text{K}^{14}\text{NO}_3$  and  $\text{K}^{15}\text{NO}_3$  as the reactant feedstocks. (h) Wavelength-dependent AQY of Cu-TNS for PCNRA under various reaction conditions. (i) Comparison of  $\text{NH}_3$  yield, selectivity, and AQY of Cu-TNS with those of previously reported PCNRA photocatalysts.

$\text{NH}_4^+$  selectivity from a photocatalytic viewpoint was also assessed by considering the total amount of reacted electrons (including  $\text{H}_2$  evolution) (Fig. S27 and Supporting Information). During the initial two hours, the  $\text{H}_2$  evolution rate from using Cu-TNS was negligible, and 99.2%  $\text{NH}_4^+$  selectivity was achieved. However, it increased considerably as  $\text{NO}_3^-$  was depleted over time, with  $\text{NH}_4^+$  selectivity eventually reaching 93.5% (Fig. S28). Hence, the  $\text{H}_2$  evolution activity of Cu-TNS was further evaluated without  $\text{NO}_3^-$  to verify the correlation between proton reduction and  $\text{NO}_3^-$  abundance (Fig. S29). As expected, the absence of  $\text{NO}_3^-$  significantly improved  $\text{H}_2$  production compared to the presence of  $\text{NO}_3^-$ , suggesting that abundant  $\text{NO}_3^-$  boosts preferential  $\text{NO}_3^-$  reduction while suppressing  $\text{H}^+$  reduction.

The long-term stability of Cu-TNS was evaluated during four consecutive reaction cycles (Fig. 3f), with  $\text{NO}_3^-$  replenishment at the end of each cycle restoring the diminished  $\text{NH}_4^+$  production rate to its initial level. A similar trend was observed without noticeable degradation for the 96-h reaction of 4 consecutive cycles, indicating that the stabilization of the Cu atoms in the  $\text{TiO}_2$  lattice leads to excellent stability, unlike typical SACs suffering from migration, aggregation, or leaching due to high surface energy [40]. Interestingly, the increase in  $\text{H}_2$  production activity also declined back to its initial level upon  $\text{NO}_3^-$  replenishment,

again supporting that  $\text{NO}_3^-$  is preferentially reduced on the catalyst surface rather than  $\text{H}^+$  (Fig. S30). The post-characterization of Cu-TNS after the long-term photoreaction provided almost identical results, thereby confirming again the excellent stability and recyclability of Cu-TNS for PCNRA (Fig. S31).

An isotopic labeling experiment using  $^{14}\text{NO}_3^-$  and  $^{15}\text{NO}_3^-$  as the feedstock was carried out to clarify the N source for the products from the PCNRA. Within 12 h of reaction using the isotopic feedstock, triplet  $^{14}\text{NH}_4^+$  and doublet  $^{15}\text{NH}_4^+$  signals were distinguishable in the  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of Cu-TNS, verifying that the supplied  $\text{NO}_3^-$  had been successfully reduced to  $\text{NH}_4^+$  (Fig. 3g). Moreover, the time-dependent increase in the NMR signals and analogous quantification of  $^{14}\text{NH}_4^+$  and  $^{15}\text{NH}_4^+$  indicate once again that prevalent  $\text{NH}_4^+$  production occurs through PCNRA, implying that the involvement of external N species was negligible (Figs. S32–S34). The produced  $\text{NH}_4^+$  amount after 12 h of the reaction was quantified using assorted methods such as NMR, IC, and colorimetry (Fig. S35). All three techniques provided comparable results and highlighted the validity of our quantification findings. Slight overestimation when using colorimetry may be ascribed to the presence of a hole scavenger reacting with the Nessler reagent [41].

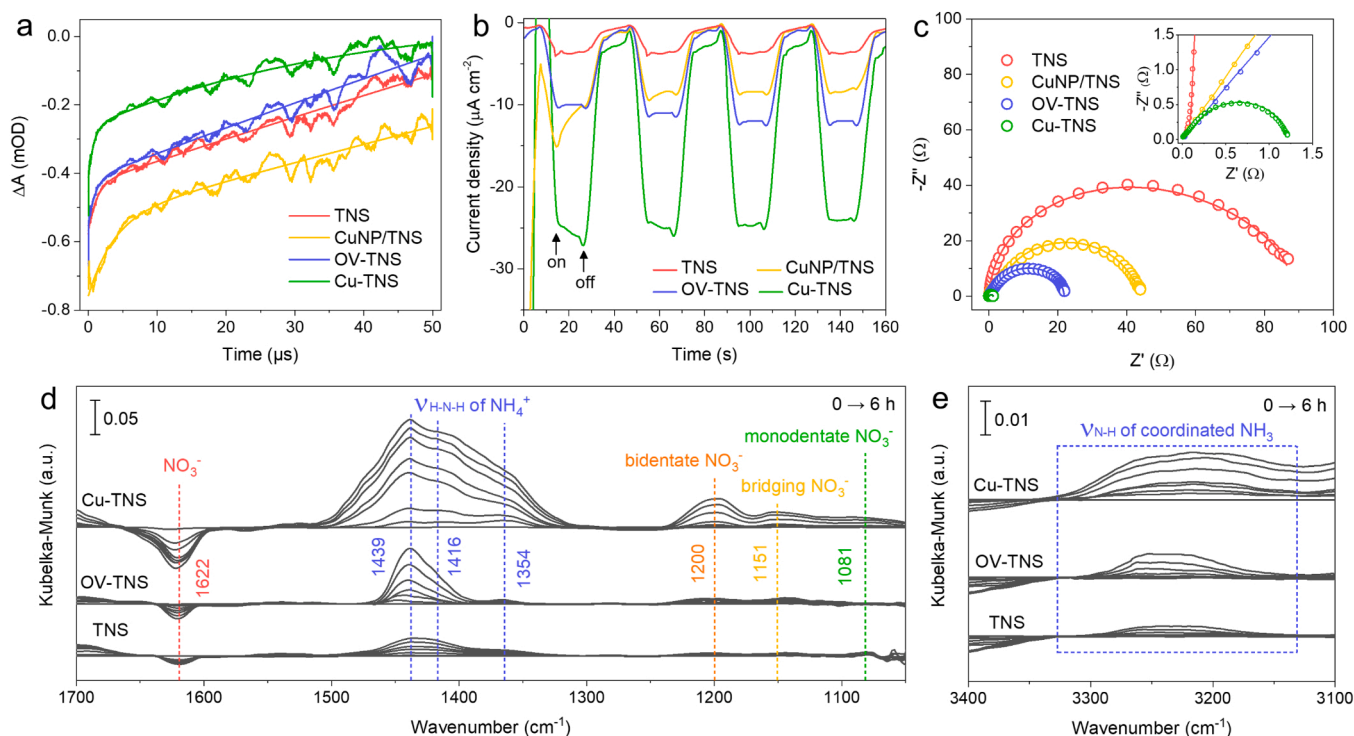
As catalytic activity is highly dependent on the reaction conditions, four sets of optimization experiments to regulate the catalyst dose,  $\text{NO}_3^-$  amount, sacrificial reagent type, and volume were carried out to maximize the photocatalytic activity and AQY of Cu-TNS (Fig. S36). Consequently, the reaction conditions of 50 mg catalyst, 500  $\mu\text{mol}$   $\text{NO}_3^-$  and 10 vol%  $\text{HCOOH}$  with which Cu-TNS achieved the highest  $\text{NH}_4^+$  production rate of 29.81  $\mu\text{mol h}^{-1}$  were found to be optimal and were subsequently selected for obtaining AQY measurements. Furthermore, 0.5 wt% (0.45 vol%)  $\text{HCOOH}$  was also considered as the organic matter content (<1 wt%) in actual waste water [42,43] (denoted as practical conditions). Compared with the initial conditions, the optimal ones comprehensively improved the AQY of Cu-TNS in the absorption region up to 700 nm under adjusted reaction conditions; the highest AQY of 11.7% at 330 nm together with a solar-to-ammonia conversion efficiency of 0.40% under the optimal conditions (Fig. 3h) shows that it far outperforms the current state-of-the-art photocatalysts for PcNRA (Fig. 3i and Table S5).

### 3.3. Charge-transfer dynamics

As the photocatalytic performance is closely related to the charge carrier transfer in the catalyst, the mechanistic origins underlying the exceptional PcNRA activity of Cu-TNS were elucidated by probing its interfacial charge dynamics. Steady-state photoluminescence (PL) emission and time-resolved PL (TRPL) spectroscopy were first employed to study the charge-transfer dynamics in the bulk phase in the catalysts (Fig. S37 and Table S6). The quenched PL emission upon the introduction of Cu or OVs suggests the emergence of non-radiative recombination pathways within TNS (electron migration to Cu or OVs). This contention was validated by the hastened PL decay kinetics (shortened average carrier lifetime) due to the presence of Cu and/or OVs, signifying that the charge-transfer dynamics of TNS are accelerated via an additional interfacial charge-transfer pathway. The overall photocatalytic performance could also be governed by the surface charge

dynamics occurring at a relatively slow timescale ( $\mu\text{s}$  to  $\text{ms}$ ) [44], which is thus the rate-determining step. In order to paint a clear picture of the surface charge dynamics, in-situ transient absorption (TA) measurements were conducted under the optimal conditions for PcNRA to uncover the actual interaction mechanism between the surface photoelectrons and the reacting species (Fig. 4a and Fig. S38). The wavelength region for the surface photoelectrons was identified as 400 nm, which showed pronounced bleaching recovery in the presence of  $\text{Ag}^+$  ions as electron scavengers (Fig. S39). Accordingly, the in-situ TA profiles probed at 400 nm were fitted with a triexponential kinetics equation for quantitative interpretation (Table S7). Notably, the three modified TNS catalysts displayed substantially faster bleaching recovery kinetics than TNS, among which Cu-TNS exhibited the most hastened kinetics for bleaching recovery with an average lifetime (26.2  $\mu\text{s}$ ), which is more than one order of magnitude shorter than TNS (526.0  $\mu\text{s}$ ). The markedly shortened lifetime of Cu-TNS demonstrates that the surface photoelectrons are expeditiously consumed to participate in the  $\text{NO}_3^-$  reduction reaction, which accounts for the exceptional PcNRA activity.

The superior photogenerated charge transfer of Cu-TNS was further revealed via a photoelectrochemical (PEC) assessment. The photoelectrode was fabricated using facile electrophoretic deposition on a conductive substrate to avoid altering the intrinsic properties of the powder photocatalysts. The prepared photoelectrode had both uniform thickness and contact with the catalyst, rendering it suitable for the PEC measurements (Fig. S40a). The linear sweep voltammetry curves of Cu-TNS exhibit enhanced current density in the presence of  $\text{NO}_3^-$ , which is indicative of its capability to reduce  $\text{NO}_3^-$  (Fig. S40b). Compared with the photoelectrodes made with its counterparts, the Cu-TNS one attained the most positive onset potential, thereby proving its superior  $\text{NO}_3^-$  reduction performance (Fig. S40c). Likewise, the transient photocurrent density of the Cu-TNS photoelectrode was substantially higher than that of its counterparts due to its higher charge-transfer rate for the surface  $\text{NO}_3^-$  reduction reaction (Fig. 4b). This consistent conclusion is also evidenced by the electrochemical impedance spectra, in which Cu-TNS



**Fig. 4.** (a) The TA kinetic profiles of the prepared photocatalysts probed at 400 nm. PEC assessment of the prepared photoelectrodes at  $-0.6$  V vs.  $\text{Ag}/\text{AgCl}$  in aqueous 0.5 M  $\text{K}_2\text{SO}_4$  solution: (b) transient photocurrent density curves under sequential irradiation with an interval of 20 s on/off switch and (c) electrochemical impedance spectroscopy Nyquist plots under continuous irradiation (inset: enlarged plots showing the full arc of Cu-TNS). *In-situ* DRIFTS spectra of Cu-TNS, OV-TNS and TNS under 6 h of light irradiation in the range of (d) 1700–1050  $\text{cm}^{-1}$  and (e) 3400–3100  $\text{cm}^{-1}$ .



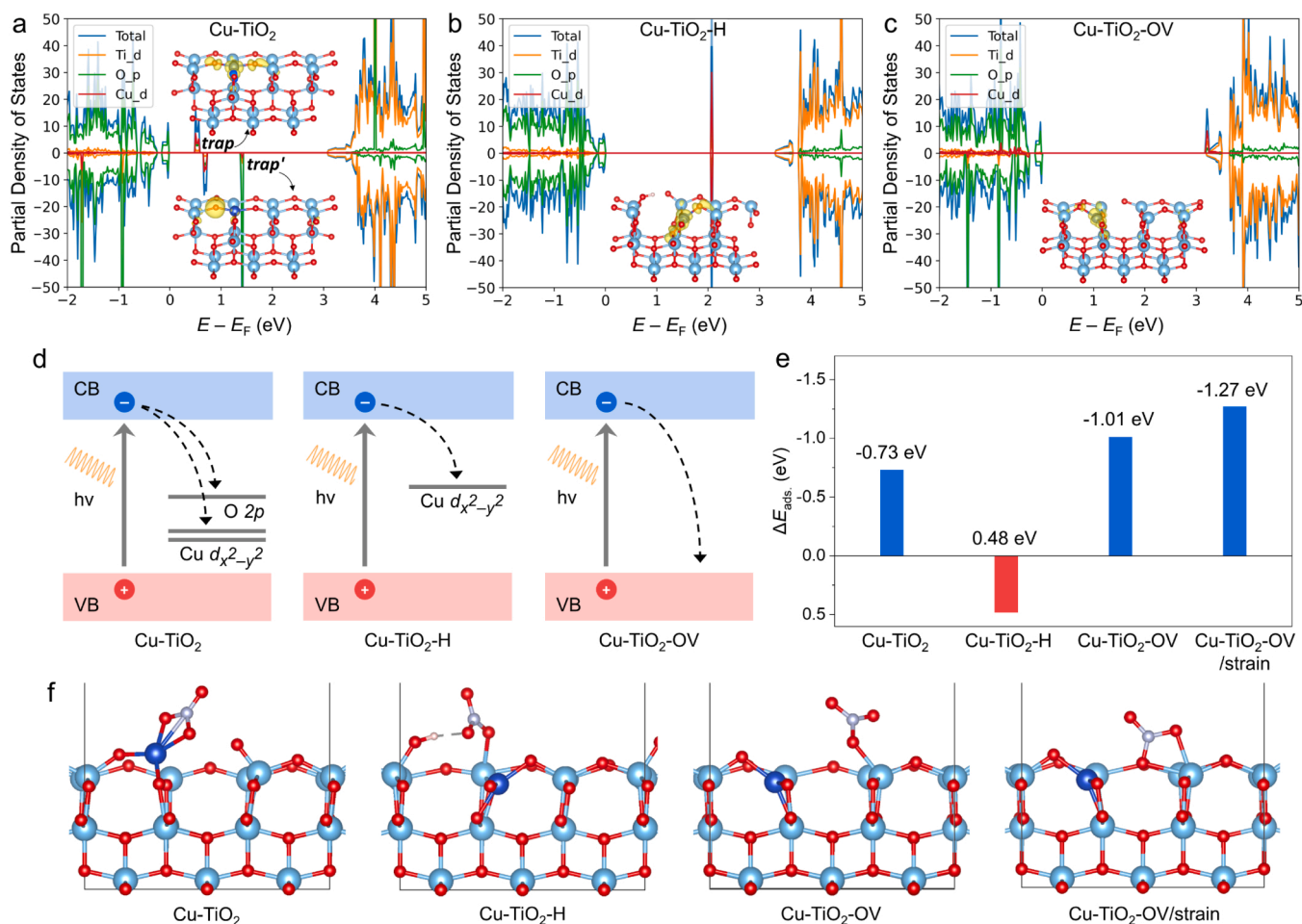
exhibits the smallest arc radius (charge-transfer resistance,  $R_{ct} = 1.22 \Omega$ ) in the subsequent Nyquist plots, thereby indicating that it provided the most effective separation of the photogenerated charge carriers (Fig. 4c, Fig. S40d and Table S8). The PEC measurements also deliver reasonable evidence for the pronounced charge transfer and the exceptional PCNRA activity of Cu-TNS under photoirradiation, which is in accordance with the above in-situ TA results.

### 3.4. Photocatalytic reaction mechanism

Afterward, to dynamically investigate the reaction mechanism of PCNRA, in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis of the  $\text{NO}_3^-$ -adsorbed catalysts was conducted under continuous irradiation. The spectra for Cu-TNS exhibit noticeable attenuation of the absorption band at  $1622 \text{ cm}^{-1}$  corresponding to the adsorbed  $\text{NO}_3^-$  species [14] whereas that in the OV-TNS spectra was only marginal and that in the TNS spectra was even less than OV-TNS (Fig. 4d). Moreover, the spectra of Cu-TNS show distinctive absorption bands at  $1200$ ,  $1151$ , and  $1081 \text{ cm}^{-1}$ , which were assigned to activated  $\text{NO}_3^-$  species in the bidentate [45], bridging [22] and monodentate [22] coordination modes, respectively. On the other hand, the TNS spectra barely show the absorption bands corresponding to the activated  $\text{NO}_3^-$  species, and the OV-TNS spectra show a slight increase in the corresponding absorption bands. These results evidently imply that the adsorption of  $\text{NO}_3^-$  is accelerated due to the presence of OV in the catalyst surface and can be readily activated for the subsequent reduction

process. Moreover, the simultaneous presence of isolated Cu atoms and OV even further stimulates this process, achieving the more hastened  $\text{NO}_3^-$  adsorption and activation. In particular, the steady and substantial increase in the absorption bands at  $1439$ ,  $1416$ , and  $1354 \text{ cm}^{-1}$  assigned to the H–N–H stretching vibration [14,22] infers the selective production of  $\text{NH}_4^+$  via PCNRA, which explicitly appeared in the spectra for Cu-TNS. The efficient  $\text{NH}_4^+$  production of Cu-TNS was also validated by a specific band in the range of  $3300\text{--}3100 \text{ cm}^{-1}$ , which is widely accepted as the N–H stretching vibration in coordinated  $\text{NH}_3$  species [46,47] (Fig. 4e). In contrast, the insignificant rise in  $\text{NH}_4^+$ -associated absorption bands in TNS reflects inferior and non-selective PCNRA activity because of no single Cu atoms and surface defects. Meanwhile, the OV-TNS spectrum shows slightly increased  $\text{NH}_4^+$ -associated absorption bands compared to TNS but considerably less than Cu-TNS, indicating the significance of isolated Cu atoms on the catalyst surface for PCNRA. Thus, the in-situ DRIFTS results firmly prove that  $\text{NO}_3^-$  is favorably adsorbed and activated in the presence of isolated Cu atoms and surface defects and then ultimately reduced to  $\text{NH}_4^+$ .

To gain deeper insight into the effect of Cu single-atoms on the enhanced photocatalytic activity, density functional theory (DFT) calculations were performed using different local geometries of the anatase  $\text{TiO}_2$  (001) surface models such as single-atom Cu-incorporated  $\text{TiO}_2$  ( $\text{Cu-TiO}_2$ ),  $\text{Cu-TiO}_2$  with OV ( $\text{Cu-TiO}_2\text{-OV}$ ) and partially hydrogenated  $\text{Cu-TiO}_2$  ( $\text{Cu-TiO}_2\text{-H}$ ) (Fig. S41). The spin-polarized projected density of states (Fig. 5a–c and Fig. S42) and the corresponding photoelectron-transfer pathway schematics (Fig. 5d) based on hybrid functional

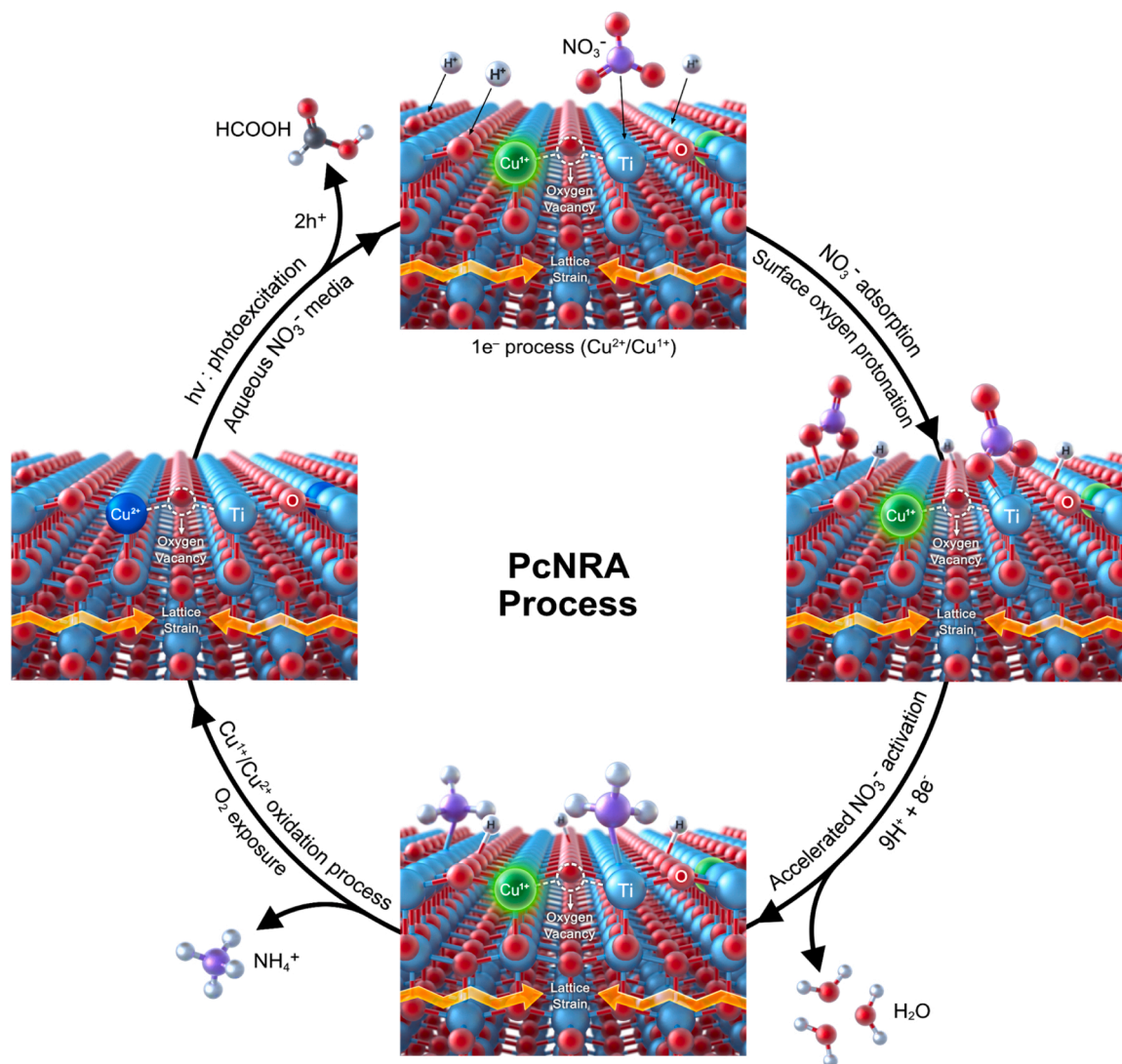


**Fig. 5.** PDOS of (a) Cu-TiO<sub>2</sub>, which contains one spin-up trap state and two spin-down trap states, (b) Cu-TiO<sub>2</sub>-H, which has a mid-gap trap state within band gap and (c) Cu-TiO<sub>2</sub>-OV, which shows the shallow trap state near CB minimum (inset: the DFT-optimized atomic structure for each state). (d) Schematics of the electron transfer process for each state after photoexcitation of charge carriers. (e) Adsorption energies and (f) configurations of  $\text{NO}_3^-$  on the anatase  $\text{TiO}_2$  (001) surface of each state.

calculations elucidate that the Cu atom in a Ti vacancy provides three trap states which were primarily derived from the O 2p orbitals (marked as *trap'*) and the Cu  $d_{x-y}^{22}$  orbital (marked as *trap*). Interestingly, when an H atom is favorably adsorbed on the two-coordinated surface O site (adsorption energy,  $\Delta E_{ads.} = -3.59$  eV) in the aqueous medium where the PcNRA reaction takes place, the spin-up and spin-down channels form one mid-gap trap state at 2.07 eV. This single mid-gap state, mainly contributed by the Cu  $d_{x-y}^{22}$  orbital, enhances the visible light absorption and accumulates the photoelectrons, leading to efficient charge separation. By contrast, only the shallow trap state was left near the CB minimum when OV was introduced at the O site neighboring the Cu atom. Moreover, the first deoxidation of  $\text{NO}_3^-$  is typically regarded as the rate-determining step in  $\text{NO}_3^-$  reduction, and thus the strength of  $\text{NO}_3^-$  adsorption on the catalyst is highly correlated with the overall reaction rate [48]. Therefore, the adsorption energies and configurations of  $\text{NO}_3^-$  on each surface model were examined as shown in Fig. 5e and f. The  $\text{NO}_3^-$  adsorption on the  $\text{TiO}_2$  (001) surface is favored in bidentate mode irrespective of local geometry, among which the Cu- $\text{TiO}_2$ -OV strongly stabilizes the  $\text{NO}_3^-$  adsorption ( $\Delta E_{ads.} = -1.04$  eV) compared to the other surfaces (Cu- $\text{TiO}_2$ ,  $\Delta E_{ads.} = -0.73$  eV and Cu- $\text{TiO}_2$ -H,  $\Delta E_{ads.} =$

0.48 eV). Notably, the  $\text{NO}_3^-$  adsorption is even further enhanced to  $-1.27$  eV when the compressive strain of 0.705% is introduced into Cu- $\text{TiO}_2$ -OV (denoted as Cu- $\text{TiO}_2$ -OV/strain). It is noteworthy that  $\text{NO}_3^-$  is favorably adsorbed on isolated Cu atoms of the Cu- $\text{TiO}_2$  surface, but favorably adsorbed on Ti atoms adjacent to Cu atoms once OV is introduced to the surface (Cu- $\text{TiO}_2$ -OV and Cu- $\text{TiO}_2$ -OV/strain). The strong and unitary site-specific  $\text{NO}_3^-$  adsorption on Ti atoms adjacent to isolated Cu atoms and OV can effectively suppress the release of the intermediate ( $\text{NO}_2$ ) during the reduction process and the multiple adsorption of  $\text{NO}_3^-$  at a single site, reducing the N-N interaction to ensure high selectivity for  $\text{NH}_3$  [14]. Our DFT results clearly demonstrate the different roles and contributions of each defect and strain induced in Cu-TNS. The H defect forms the mid-gap state promoting the light absorption and the charge separation, while OVs and strain enhance the  $\text{NO}_3^-$  adsorption.

Here, the PcNRA reaction mechanism on Cu-TNS is proposed on the basis of the aforementioned analyses (Fig. 6). Initially,  $\text{TiO}_2$  generates electron-hole pairs under light irradiation. The photogenerated holes, which are readily consumed for organic pollutant decomposition (e.g.,  $\text{HCOOH}$ ), facilitate the reaction kinetics. Meanwhile, the aqueous



**Fig. 6.** PcNRA process mechanism on Cu-TNS.  $\text{TiO}_2$  with isolated  $\text{Cu}^{2+}$  atomic sites (blue) and defects generate photoexcited electrons and holes under light irradiation. The photogenerated holes are consumed by  $\text{HCOOH}$  while the photoelectrons are localized at the Cu sites, reducing  $\text{Cu}^{2+}$  to  $\text{Cu}^{1+}$  (green glow).  $\text{NO}_3^-$  is adsorbed site-specifically on the  $\text{TiO}_2$  surface in which oxygen is protonated by the aqueous medium. Defects accelerate the activation of  $\text{NO}_3^-$ , which is readily reduced to  $\text{NH}_3$  via the  $9\text{H}^+ + 8e^-$  processes. The  $\text{NH}_3$  is desorbed and preserved in the ionized form of  $\text{NH}_4^+$  in an aqueous medium.  $\text{O}_2$  purging in the dark restores the Cu valence to its initial state.

medium easily protonates the surface oxygen, leaving a single trap state contributed by the *d* orbitals of the isolated Cu atoms. The electrons migrate from the CB of TiO<sub>2</sub> and become specifically localized in the  $d_{xy}^{22}$  state of the isolated Cu atoms. Thus, efficient charge separation occurs and the accumulated electrons tune the valence state of the Cu atoms and optical modulation occurs. The defects configured adjacent to the Cu atoms induce strong site-specific adsorption of NO<sub>3</sub><sup>-</sup>, reducing the possibility of N–N bonding (an interaction between liberated intermediates) and promptly activating them into the bidentate coordination mode. The coordinated NO<sub>3</sub><sup>-</sup> is reduced to NH<sub>3</sub> and H<sub>2</sub>O is released via 9 H<sup>+</sup> and 8 e<sup>-</sup> processes, which ultimately ionize to form NH<sub>4</sub><sup>+</sup> in an aqueous medium. The changed valence state of Cu atoms can be simply restored by exposure to O<sub>2</sub> without light irradiation. Consequently, the efficient charge separation and facilitated NO<sub>3</sub><sup>-</sup> adsorption/activation synergistically accelerate the NO<sub>3</sub><sup>-</sup> reduction kinetics to effectively photosynthesize NH<sub>3</sub>.

#### 4. Conclusion

We report a highly active and photochemically stable Cu-TNS photocatalyst for selective NH<sub>3</sub> production via NO<sub>3</sub><sup>-</sup> reduction under ambient conditions. A simple solvothermal method successfully distributed single Cu atoms into Ti vacancies in the TiO<sub>2</sub> matrix, spontaneously forming defects such as OV and lattice strain due to the different valence states and sizes of Ti and Cu. The isolated and stabilized Cu atomic sites accumulate photoelectrons, which inhibits charge carrier recombination and allows more electrons to participate in the reduction reaction, while the structural defects eliminate the NO<sub>3</sub><sup>-</sup> activation barrier, which facilitates the reduction reaction. Evidence from a series of experiments together with DFT calculations strongly supports the synergistic effect of single Cu atoms and spontaneously formed structural defects in the TiO<sub>2</sub> lattice in terms of enhanced light absorption, efficient charge separation and accelerated NO<sub>3</sub><sup>-</sup> adsorption/activation. The Cu-TNS photocatalyst achieved 97.6% selectivity for NH<sub>3</sub>, a 62-fold enhancement in catalytic activity over TNS, an AQY of 11.7% at 330 nm and a solar-to-ammonia conversion efficiency of 0.40% for NH<sub>3</sub> photosynthesis. Our investigation clearly demonstrates for the first time the impressive impact of SAC along with defect formation on PCNRA, thereby providing the future landscapes of green NH<sub>3</sub> production.

#### CRediT authorship contribution statement

**Hyun Sik Moon:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Byeongju Song:** Investigation, Validation. **Jiwon Jeon:** Investigation, Writing – original draft. **Ting-Hsuan Lai:** Investigation, Writing – original draft. **Yu-Peng Chang:** Investigation, Writing – original draft. **Yi-Dong Lin:** Investigation. **Jun Kue Park:** Investigation, Validation, Formal analysis, Writing – original draft. **Yan-Gu Lin:** Formal analysis, Validation. **Yung-Jung Hsu:** Formal analysis, Validation, Writing – review & editing. **Hyeyoung Shin:** Formal analysis, Validation, Writing – review & editing. **Yongju Yun:** Formal analysis, Validation, Data curation. **Kijung Yong:** Supervision, Funding acquisition, Project administration, Writing – review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data Availability

Data will be made available on request.

#### Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (NRF-2021R1A5A1084921, NRF-2021K1A4A8A02079226).

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.123185](https://doi.org/10.1016/j.apcatb.2023.123185).

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